

SPEAKERS

"Activation of Superoxide Ion by Organic and Metallo Coupling Reactions"

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Reduction of O_2 to superoxide ion (O_2^-) in the presence of protons and transition metal ions yields highly reactive perhydroxyl and peroxide intermediates. Likewise, reduction of dioxygen in the presence of activating substrates (alkyl halides, esters, methyl viologen, and transition metal complexes) results in a concerted two-electron process to yield reactive oxygenating agents. The interaction of O_2 and its reduction products with iron-porphyrins yields a variety of reactive intermediates; several adducts are further activated by reduction. Several examples will be discussed of the oxidation of organic and inorganic substrates via reductive activation of O_2 .

Oxygen Activation by Heme-Containing Oxygenases.

Evidence for Free Radical Processes.

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An understanding of the details of oxygen activation and transfer mediated by heme-containing oxygenases has been frustrated by the transient nature of reactive intermediates in the catalytic cycle. Recent results pertaining to the mechanism of cytochrome P-450 will be described. Specifically designed, diagnostic substrate molecules are employed to reveal the nature of the ultimate, heme-centered oxidant. In another approach, synthetic models of the heme site of cytochrome P-450 have been constructed to provide mechanistic precedents in simple molecular systems.